

09-05-000

PTO/SB/05 (4-98)

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Attorney Docket No. 011916.107912

First Inventor or Application Identifier PASZKOWSKI

Title SYSTEM AND METHOD FOR PRODUCING HIGH
PURITY COLLOIDAL SILICA AND POTASSIUM

HYDROXIDE

Express Mail Label No. EL597574428US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: Assistant Commissioner for Patents
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1. ☒ * Fee Transmittal Form (e.g., PTO/SB/17)
(Submit an original and a duplicate for fee processing)
2. ☒ * Specification (Total Pages 17) 1
(preferred arrangement set forth below)
- Descriptive title of the invention
 - Cross References to Related Applications
 - Statement Regarding Fed sponsored R & D
 - Reference to Microfiche Appendix
 - Background of the Invention
 - Brief Summary of the Invention
 - Brief Description of the Drawings (if filed)
 - Detailed Description
 - Claim(s)
 - Abstract of the Disclosure
3. ☒ Drawing(s) (35 U.S.C. 113) (Total Sheets 8) 1
4. Oath or Declaration (Total Sheets 1) 1
- a. ☒ Newly executed (original or copy)
- b. ☐ Copy from a prior application (37 C.F.R. § 1.63(d))
(for a continuation/divisional with Box 18 completed)
- i. ☐ DELETION OF INVENTOR(S)
Signed statement attached deleting
inventor(s) named in the prior application,
see 37 C.F.R. §§ 1.63(d)(2) and 1.63(b).

5. ☐ Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission
(if applicable, all necessary)
- a. ☐ Computer Readable Copy
- b. ☐ Paper Copy (identical to computer copy)
- c. ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

7. ☒ Assignment Papers (cover sheet & document(s))
8. ☐ 37 C.F.R. § 3.73(b) Statement (when there is an assignee) ☐ Power of Attorney
9. ☐ English Translation Document (if applicable)
10. ☒ Information Disclosure Statement (IDS/PTO-1449) ☐ Copies of IDS Citations
11. ☐ Preliminary Amendment
12. ☒ Return Receipt Postcard (MPEP 503)
(Should be specifically itemized)
- *Small Entity
13. ☒ Statement(s) ☒ Statement filed in prior application,
(PTO/SB/09-12) Status still proper and desired
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16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:

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17. CORRESPONDENCE ADDRESS

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PATENT AND TRADEMARK OFFICE

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Aug-01-2002 10:11 am From: ROUTAWAN SANDERS

T-77C P 003/003 P-837

PTO-SM-10 (1-99)

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(37 CFR 1.9(f) & 1.27(c)) SMALL BUSINESS CONCERN**Docket Number (Optional)
011916.107912Applicant, Patentee, or Identifier: Andrew Joseph Paszkowski

Application or Patent No.:

Filed or Issued:

Title: SYSTEM AND METHOD FOR PRODUCING HIGH PURITY COLLOIDAL SILICA AND POTASSIUM HYDROXIDE

I hereby state that I am

☐ the owner of the small business concern identified below;☒ an official of the small business concern empowered to act on behalf of the concern identified below.NAME OF SMALL BUSINESS CONCERN Chemical Products CorporationADDRESS OF SMALL BUSINESS CONCERN P.O. Box 2470, 102 Old Mill Road, SE
Cartersville, Georgia 30120

I hereby state that the above identified small business concern qualifies as a small business concern as defined in 13 CFR Part 121 for purposes of paying reduced fees in the United States Patent and Trademark Office. Questions related to size standards for a small business concern may be directed to: Small Business Administration, Size Standards Staff, 409 Third Street, SW, Washington, DC 20416

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☐ the application identified above
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NAME OF PERSON SIGNING

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TITLE OF PERSON IF OTHER THAN OWNER

SECRETARY & LEGAL COUNSEL

ADDRESS OF PERSON SIGNING

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SIGNATURE

C.F. Doggatt

DATE

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0613678/01

Patent
Customer No.: 006980
Express Mail No. EL597574428US
Express Mail Date: September 1, 2000
Document No. 610859.02
Attorney Docket No.: 011916.107912

**APPLICATION FOR LETTERS PATENT
UNITED STATES OF AMERICA**

Be it known that I, Andrew Joseph Paszkowski, a citizen of the United States of America, residing at 3802 Halisport Lane NW, Kennesaw, Georgia, 30152, US, have invented certain new and useful improvements in a

**SYSTEM AND METHOD FOR PRODUCING HIGH PURITY COLLOIDAL SILICA
AND POTASSIUM HYDROXIDE**

of which the following is a specification.

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SYSTEM AND METHOD FOR PRODUCING HIGH PURITY COLLOIDAL SILICA AND POTASSIUM HYDROXIDE

The invention relates generally to the fields of ion exchange, ultrafiltration and
5 electrodialysis and, more specifically, to the methods for utilizing ion exchange, ultrafiltration
and electrodialysis to produce high purity colloidal silica and/or potassium hydroxide.

BACKGROUND OF THE INVENTION

Colloidal silica is a suspension of very small, spherical particles of amorphous (not
crystalline) silica suspended in water. The material is colloidal in that the silica particles do
10 not settle out of the solution. The silica particles generally range in size from about 8
nanometers to a maximum size of about 80 nanometers, beyond which the silica ceases to be
colloidal and begins to settle out of solution. Colloidal silica has been used for a variety of
purposes, including precision casting, as a lining for molds, as a frictionizing (non-skid)
agent, and in a variety of medical and pharmaceutical uses such as toothpaste, dental castings
15 and drug delivery systems.

One relatively recent use which has arisen for colloidal silica is in the polishing of
semiconductor materials, such as the silicon wafers used in computer chips, by a process
known as Chemical Mechanical Planarization (CMP). CMP involves the polishing of
semiconductors and chips using very small abrasive particles of silica alumina, ceria or other
20 materials in a slurry or suspension with a chemically active carrier solution. Colloidal silica
has also recently come into use in polishing other items such as hard disk drives, electronic
memory devices and raw silicon oxide wafers to accomplish the rough polishing of chips
prior to CMP.

The electrical performance of finished semiconductor chips can easily be affected by
25 contaminants to which the semiconductor wafers are exposed during processing. Such
contamination can be in the form of discrete particles and water soluble or dispersed organic
and inorganic impurities. In particular, the use of silica sols that are contaminated with trace
transition metals, alkali and alkaline earth metals, aluminum, and other metals causes
difficulties when used in wafer polishing. Sodium, potassium, alkali and alkaline earth
30 metals such as calcium, magnesium, and transition metals such as iron, copper, manganese,
nickel, and zinc are particularly troublesome. In general, any transition metal from groups
IB, IIB, IIIB, IVB, VB, VIB, and group VIII of the Periodic Table of Elements, if present in
high enough concentrations, can cause difficulties in the final products manufactured with
silica sols containing these contaminants.

An additional problem of metal contaminants is that many of these substances have much higher diffusivities in both silicon and silicon dioxide than do the more conventional dopants, such as phosphorus and boron. As a result unpredictable electrical properties can result when silicon wafers are contaminated with these metals. For example, alkali metals
5 such as lithium, sodium, and potassium cause shifts in electrical properties (threshold and flat-band voltages) when incorporated into semiconductor devices.

Currently used colloidal silica CMP slurries generally include a relatively high amount of contaminating sodium, which is very difficult to remove. The contaminating sodium causes defects in the chips in the later manufacturing processes. Accordingly, there is
10 a need for an improved method for producing very low sodium content colloidal silica for use in these applications. There is also a need for an improved method of producing high purity potassium hydroxide which is also an additive used in some CMP slurries.

One method which has been developed in an attempt to produce a low sodium potassium stabilized silica sol is disclosed in U.S. Patent No. 4,915,870 to Jones. The method disclosed by Jones uses an acid sol process to produce a silica sol having a sodium
15 concentration of less than 150 ppm using commercially available KOH to stabilize the pH of the sol. However, while the method disclosed by Jones is suitable for producing silica sols having a sodium concentration of less than 150 ppm, it would be preferable to produce silica sols having much lower sodium concentrations for use in electronics applications.

Therefore, it is an object of the present invention to provide a system and method for producing very low sodium colloidal silica suitable for use in electronic applications.

It is another object of the present invention to provide a process for producing colloidal silica particles having a uniform shape and size.

It is yet another object of the present invention to provide a method for producing
25 very high purity potassium hydroxide for use in the CMP slurry, and other uses.

BRIEF DESCRIPTION OF THE INVENTION

The above objectives are accomplished according to the present invention by providing a system and method for producing high purity colloidal silica which includes the steps of providing a quantity of potassium silicate; subjecting the quantity of potassium
30 silicate to an ion exchange process to remove a first portion of potassium therefrom to produce a quantity of colloidal silica; and subjecting the quantity of colloidal silica to ultrafiltration to remove a portion of sodium therefrom, producing a quantity of high purity colloidal silica.

In a further preferred embodiment of the present invention, the ion exchange resin which has previously been utilized to remove potassium from the potassium silicate may be utilized in the production of high purity potassium salts. To produce a very low sodium, high purity potassium salt, the ion exchange resin may be regenerated by contacting it with an acid to produce a quantity of potassium salt, which may be further purified by evaporation, crystallization and/or ultrafiltration. The low-sodium potassium salt produced is further processed by electrodialysis and/or electrolysis in order to produce a low-sodium potassium hydroxide, suitable for re-addition to the low-sodium colloidal silica to produce a very low sodium potassium hydroxide stabilized CMP silica slurry.

Other objects, aspects, and advantages of the present invention will be apparent to those skilled in the art from a reading of the following detailed disclosure of the invention.

BRIEF DESCRIPTION OF THE FIGURES

The construction and design to carry out the invention will hereinafter be described together with other features thereof. The invention will be more readily understood from a reading of the following specification and by reference to the accompanying drawings forming a part thereof, wherein an example of the invention is shown and wherein:

FIG. 1 is a block diagram illustrating a preferred embodiment of the method of the present invention.

FIG. 2 is a block diagram illustrating the membrane configuration used in a first set of electrodialysis experiments.

FIG. 3 is a block diagram illustrating the membrane configuration used in a second set of electrodialysis experiments.

FIG. 4 is a table summarizing data from KOH production experiments using electrodialysis.

FIG. 5 is a first table summarizing partition coefficient data from electrodialysis experiments.

FIG. 6 is a second table summarizing partition coefficient data from electrodialysis experiments.

FIG. 7 is a first table summarizing KOH production data from electrolysis experiments.

FIG. 8 is a first table summarizing KOH production data from electrolysis experiments.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now in more detail to the drawings, the invention will now be described in detail. As shown in FIG. 1, a quantity of silicate salt is subjected to an ion exchange process in an ion exchange reactor 22 wherein the metallic cation is removed to produce a colloidal silica sol and a cation enriched ion exchange resin. The silica sol is then subjected to ultrafiltration in ultrafiltration device 24 removing residual traces of the metallic cation and concentrating the solids to produce a high purity colloidal silica sol. This silica sol is particularly suitable for use as a CMP slurry. The cation enriched resin is then regenerated by the addition of acid in regeneration chamber 26 to produce a salt of the metallic cation. The resulting metallic cation salt is purified, first by concentration in evaporator/crystallizer 28 followed by electrodialysis in electrodialysis cell 30 to produce a high purity metal hydroxide, preferably KOH, also suitable for sale on the open market for use in CMP slurries.

The formation of colloidal silica in the present invention is accomplished by subjecting a quantity of low-sodium silicate salt to an ion exchange process in an ion exchange reactor 22. In the preferred embodiment, the silicate salt used is a potassium silicate having a sodium concentration of less than 200 ppm and more preferably less than 100 ppm, though one of ordinary skill in the art should recognize that other silicate salts, such as lithium silicate, magnesium silicate, and calcium silicate may also be suitable. A potassium silicate having less than 100 ppm sodium which has proven suitable is Zacsil E-200 from Zaclon, Inc. of Cleveland, OH. Because the initial silica salt used has a low sodium level, the resultant colloidal silica products also have a very low level of contaminating sodium in the range of 1-5 ppm. This sodium level may be further reduced by washing the colloidal silica with deionized water in an ultrafiltration device 24 while adding potassium hydroxide to maintain the pH and cation concentration. The resulting product is a colloidal silica sol, based in potassium hydroxide which includes less than 1 ppm contaminating sodium, a purity much higher than is obtainable by conventional processes.

One method of producing a colloidal silica sol having a substantially uniform particle size is disclosed in U.S. Patent No. 3,789,009 to Irani. The sols are produced by adding simultaneously an alkali metal silicate and a cation exchange resin to a heel of water containing preformed colloidal silica particles at a pH within the range of 8-11, at a temperature of 60-150 degrees Celsius, and at a rate below that at which nucleation occurs. The cation exchange resin is added to the heel to remove the alkali metal cations from the alkali metal silicate causing the silicic acid to polymerize onto the heel nuclei to form large

silica sols. Since the polymerization rate is similar for all of the uniform seed particles, the resulting larger sols also have a relatively uniform size distribution. By controlling the amount of alkali metal silicate and resin added it is possible to produce colloidal silica particles having a uniform size of between 8 nm and 200 nm. In this process, preferably the silicic acid concentration is maintained below the nucleation point to avoid the formation silica particles not sharing in the uniform size. Other processes to produce such sols are well known in the art.

The silica sols are then concentrated by either evaporation or, more preferably, ultrafiltration to recover an aqueous colloidal silica sol containing 5%-55% by weight SiO_2 and having a pH of between 8 and 10.5. In the preferred embodiment ultrafiltration is used to wash out contaminating sodium by replacing the aqueous solution with deionized or distilled water while simultaneously adding a small amount of ultrapure potassium hydroxide to maintain the pH. Ultrafiltration is also useful to concentrate the colloidal silica sol to a desired concentration. The resulting colloidal silica sol also optimally has a sodium concentration of less than 10 ppm sodium, but more preferably, less than 1 ppm sodium. The silica sols generally have an average particle size of 8-200 nm and preferably of from 10-80 nm and a particle size distribution with coefficient of dispersion of 0.16-0.5 and preferably 0.16 to 0.25. These sols exhibit long-term stability.

When using potassium silicate as the silicate salt, the colloidal silica process produces a waste stream of potassium salt upon acid regeneration of the ion exchange resin in regeneration chamber 26. The potassium salt waste stream is useful as a source from which high purity potassium salts may be generated. In the presently preferred colloidal silica process described above, the acid used is sulfuric acid and the waste stream has a potassium sulfate concentration of approximately 5-10%. The following example, for example and not limitation, will be directed to use of potassium sulfate. Hydrochloric acid may also be used, however, the resulting chloride contamination can create problems if the potassium products are intended to be used in the semiconductor industry. Nitric and phosphoric acids are also acceptable.

As shown in FIG. 1, to purify the potassium sulfate stream, the potassium sulfate waste is first directed to an evaporator/crystallizer 28. Evaporator/crystallizer 28 concentrates the potassium sulfate under conditions wherein potassium sulfate is only marginally soluble and, thus, preferentially crystallizes. Next, the resulting potassium sulfate crystals are redissolved in deionized water and fed into an electrodialysis cell 30 wherein the sulfate is

dialyzed out to create a very pure but weak solution of potassium hydroxide. Alternatively, the potassium sulfate solution may be separated by electrolysis. The resulting potassium hydroxide solution may then be concentrated by evaporation to produce a commercial grade ultrapure potassium hydroxide which is suitable for use in electronic applications. Currently, electronic applications require potassium hydroxide having less than ~100 ppm to 200 ppm of contaminating sodium, whereas the current process is intended to produce potassium hydroxide having less than 100 ppm contaminating sodium, but more preferably less than 10 ppm.

In the preferred embodiment, electrodialysis (ED) is used to split the potassium sulfate and produce potassium hydroxide by using a three compartment cell incorporating bipolar membrane technology. In this process, the potassium sulfate stream is circulated through the middle compartment of the cell. Due to the potential field, potassium ions are transported across the cation exchange membrane and sulfate ions are transported across the anion exchange membrane. The potassium ions then combine with hydroxide ions formed by the dissociation of water at the cathodic surface of the bipolar membrane, and the sulfate ions combine with protons formed by dissociation of water at the anodic surface of the bipolar membrane. The net result is a depletion of the potassium sulfate stream in the middle compartment and the generation of separate sulfuric acid and potassium hydroxide streams in the two adjacent compartments.

In an alternative embodiment, the potassium sulfate may be split by subjecting the KOH solution to electrolysis in a standard two compartment cell to produce electronics grade KOH. The dialysis is achieved by circulating KOH on both sides of the cell and separated by a Nafion® membrane. On the anode side of the cell oxygen gas and protons are produced. On the cathode side, hydrogen gas and hydroxyl ions are the products. The hydroxyl ions would combine with the potassium ions that cross the membrane to produce KOH. The membrane preferentially transports potassium over sodium because the concentration of potassium is much higher than that of sodium and also because the partition coefficient of potassium into Nafion® is about three to four times that of sodium. The net result is a concentrated KOH solution with very low sodium concentration.

This low-sodium KOH produced according to the above method is suitable for addition to the low sodium colloidal silica previously described to produce a KOH stabilized CMP silica slurry suitable for use in semiconductor applications. In general, the electronics industry currently prefers to use CMP silica stabilized with KOH to a pH of 10-11, which

requires addition of approximately 0.2-0.5% KOH. Electronics grade KOH has approximately 200 ppm contaminating sodium. Accordingly, if electronics grade KOH is used, the use of electronics grade KOH will result in a final CMP silica having greater than 1.0 ppm contaminating sodium. By using the very low sodium KOH of the present invention, the final sodium level of the KOH stabilized colloidal silica can be kept below 1.0 ppm, which is much more suitable for use in semiconductor applications.

Experimental Procedure

Silica Sol Synthesis

Example 1.

A colloidal silica sol was produced generally in accordance with the methods outlined in US patent number 2,631,134 to Iler et al.. Approximately 3 liters of Purolite C-106 cation exchange resin in the hydrogen form was suspended in 10 liters of deionized water in an agitated 5 gallon vessel and heated to 95 degrees Celsius. To this was rapidly added a volume of Zacsil E200 potassium silicate sufficient to deplete the ion-exchange resin, ending up with a final pH of 8.93. In this instance, 3,950 grams of the potassium silicate solution were required. The resulting colloidal suspension had an average particle size of 10.95 nanometers in diameter and a ratio of SiO_2 to K_2O of 38.

A portion of this material was then further treated with the same type of potassium silicate and ion-exchange resin according to the method taught by US patent No. 3,789,009 to Irani. The purpose of this process is to increase the particle sizes of the silica through accretion of active silica onto a heel of smaller particles, or nuclei. In this fashion, the particles can be

"grown" to 300 nanometers, or more, if desired. Twenty-five (25) gallons of material with an average particle size of 70 nanometers was produced. At this point, the material contained approximately 10% silica solids by weight.

The dilute sol was then concentrated, using an ultrafiltration unit, as is well known in the industry. In this fashion, the material was concentrated to approximately 35% SiO_2 .

When measured by atomic absorption, this suspension had a total sodium content of 8.3 parts per million. This included sodium in the carrier solution as well as any which may have been occluded within or adsorbed upon the silica particles themselves.

The ultrafiltration unit has the further desirable characteristic of removing dissolved species, such as salts along with the water in the permeate. This principle may be used to effect a process commonly referred to as diafiltration, or the dilution and removal of impurities through filtration. Once the material had been concentrated, five gallons of deionized water were added and the ultrafiltration continued in order to dilute and remove the sodium impurities. Once five gallons more permeate had been removed, which took 15-20 minutes, five more gallons of deionized water was added. This process was repeated until 50 gallons of water had been added to the suspension and 50 gallons of additional permeate had been removed. The pH of the suspension was maintained between 9 and 10 using commercially available reagent grade potassium hydroxide. When measured by atomic absorption, this suspension had a total sodium content of 0.6 parts per million in a product with a final concentration of 30% silica.

Reagent grade potassium hydroxide with a sodium content of approximately 100 ppm was added to the suspension for stability. The resultant slurry, suitable for use in CMP, had a total sodium content of 2.2 ppm. It is estimated that, with potassium hydroxide produced as described herein, the total sodium content would not exceed 1.0 ppm.

Example 2

The initial sol from example one above was used to produce a sol with an average particle size of 130 nanometers in diameter. As before, the accretion process taught by US patent No. 3,789,009 to *Irani* was used to effect the particle growth.

The same process of ultrafiltration/diafiltration described in example one was used to concentrate the suspension and to dilute and remove dissolved impurities. In this case, the process started with 30 gallons of dilute sol, concentrated to about 35% solids. At this point, the sodium content was measured by AA to be 12.9 ppm. 60 gallons of diluting water was used, as described in example one, five gallons at a time. The final solution was measured at 1.2 ppm sodium content. When the reagent grade potassium hydroxide was added, the resultant 30% SiO₂ product contained 2.2 ppm sodium.

Example 3

A solution of 5% sulfuric acid was used throughout the experimental proceedings to regenerate the ion-exchange resin. During the regeneration process, the acid strips the potassium out of the resin. The result is a solution containing approximately 5-10% potassium sulfate at a pH of about 3-4. This potassium sulfate solution was collected after

each regeneration and brought up to pH 7 using reagent grade potassium hydroxide. A total of 55 gallons was collected with an average potassium sulfate concentration of 7.0% by weight.

This material was concentrated to the point of crystallization using three four-liter open beakers. After cooling to room temperature, the crystals of potassium sulfate were separated from the mother liquor using a buchner funnel. The crystals were rinsed once with deionized water. The rinsate was collected and added to the mother liquor. It is estimated that approximately 50% of the potassium sulfate ended up as solid crystal and 50% was retained in the mother liquor.

A representative sample of the crystal was dissolved in deionized water to form a saturated solution at room temperature. The sodium content of both this solution and the mother liquor was measured using atomic absorption. The mother liquor had a sodium level of approximately 400 ppm. The solution made from dissolved crystal had a sodium content of approximately 8 ppm.

Both of these sources of potassium sulfate were sent to the Electrosynthesis Company of Lancaster, NY to perform the electro-dialysis experiments.

Electrodialysis

Electrodialysis experiments were conducted in two separate electrodialysis cells. In the first set of experiments, a Eurodia EUR 2-C-5 stack was used. The stack had a platinized titanium anode and stainless steel cathode. The gaskets were made of an ethylene-propylene terpolymer (EPDM). The effective unit surface area in this stack is 0.02m^2 . Neosepta ACM anion exchange membranes, CMB cation exchange membranes and BP-1 bipolar membranes were utilized and were arranged as shown in Figure 2.

In the second set of electrodialysis experiments, an Electrosynthesis ED-I-BP stack was used. This stack also had a platinized titanium anode and stainless steel cathode. The effective unit surface area of this stack is 0.01m^2 . The membranes used in this stack were the same as used in the Eurodia stack and were arranged as shown in Figure 3. Most components of the stack (frames, gaskets and bipolar membranes) were soaked in a dilute KOH solution prepared from reagent grade pellets for several hours before the stack was built.

The electrodialysis setup consisted of a 3.5L polyethylene feed reservoir, a 1L PTFE base reservoir, and 2L glass reservoirs for both electrode rinse and acid streams. Dilute KOH solution was circulated through the base loop for several hours to remove any traces of contamination before the commencement of the experiments. The flow rate and stack inlet

pressure of the feed loop was monitored during the run. The pressures on the other loops were set equal to that of the feed loop. All experiments were run at a constant current with the current gradually ramped up to the target current and left there for the duration of the experiment. Power was supplied by a Sorenson #DCS 20-50 power supply and total charge measured using an ESC #640 coulometer.

The electro dialysis experiments were conducted in an Electro MP cell (Electrocell AB, Sweden) equipped with nickel electrodes and a Nafion 450 cation exchange membrane. This membrane is composed of a 1200 equivalent weight polymer and is typically used for KOH production. Power was supplied by a Xantrex #XFR12-100 power supply. All components of the cell (PVDF frames, EPDM gaskets, membrane) were soaked in dilute KOH solution prepared from reagent grade pellets for several hours before the cell was built. In addition, dilute KOH was circulated through both sides of the cell for several hours to remove any traces of contamination. Both anolyte and catholyte reservoirs were HDPE and were connected to the cell via teflon tubing. The starting anolyte solution was prepared from reagent grade KOH pellets.

Initial and final samples of the acid, base, and feed streams from the electro dialysis experiments were stored in polyethylene bottles. Selected samples were analyzed for sulfate by ion chromatography, potassium and sodium content by atomic absorption, and acidity or alkalinity by acid/base titration. Samples collected from the electro dialysis experiments were also stored in polyethylene bottles and analyzed for sodium content by atomic absorption and alkalinity by acid/base titration.

A typical ED experiment was conducted as follows; 3.5 liters of a saturated solution was first prepared by dissolving K_2SO_4 crystals into deionized water. The resultant solution was then filtered through a 5 micron millipore filter before being introduced into the feed reservoir. When the high sodium saturated solution was used, it too was filtered through a 5 micron filter prior to use. The initial base consisted of 500ml deionized water. The initial acid solution and electrode rinse both consisted of one liter of nominally 0.5M sulfuric acid. The electrode rinse was reused for subsequent experiments.

After introduction of the solutions into their respective reservoirs, the circulating pumps were turned on. After several minutes of circulation, the base compartment was sampled and then the power supply started. The current was slowly ramped up to the target current. In most cases, enough charge was passed to theoretically reduce the feed concentration by 50%. At the end of the experiments the current was turned off, the solutions

drained and their volumes measured. Measured volumes of water rinses were then introduced into the acid and base compartments of circulated for several minutes before being drained and analyzed. From this analysis, the dead volumes in the compartments were calculated and added to the total volumes before calculating efficiencies etc. All samples were then analyzed as described previously. Prior to starting the next experiment, the feed, acid, and base compartments were rinsed several times with deionized water.

The electrolysis experiments were conducted as follows: The starting anolyte for the first experiment was 2.5M KOH prepared from reagent grade pellets. The starting catholyte was initially deionized water but this was changed to approx. 0.1M KOH when no current flowed at the maximum applied voltage. After the solutions were introduced into their respective reservoirs, the circulating pumps were turned on and after circulation for a few minutes, the catholyte was sampled. The power was then turned on and enough charge passed to reduce the anolyte alkalinity by about 50%. At the end of the run the cell was drained, the volumes measured and the anolyte and catholyte compartments rinsed with known amounts of deionized water for later calculation of dead volume. The second electrolysis experiment was similar with the exception that the starting catholyte was the end catholyte from the previous experiment.

The current efficiency for KOH production for all of the ED experiments (see FIG. 4) varied between 82% and 87%, with the main inefficiency being the back migration of hydroxyl ions across the cation exchange membrane. It is also possible that proton transport from the acidified feed compartment contributed to the inefficiency. The strength of KOH produced varied between 2.33M (11.6% w/w) and 3.55M (17.2% w/w)

The current efficiency for acid production averaged 78% for the two experiments with the Eurodia stack. The current efficiencies obtained with the ED-IBP stack started at 76% for the first experiment then dropped down to 50% for the third and final experiment. In all cases loss in current efficiency is due primarily to the back migration of proton from the acid compartment across the anion exchange membrane (the pH of the feed dropped in all experiments). It is also possible that part of the inefficiency is due to the diffusion of sulfuric acid molecules out of the acid compartment into the feed compartment. The initial efficiencies observed are consistent with what can be expected for this type of anion exchange membrane. The deterioration of the acid current efficiency should be evaluated over a longer time period before drawing any final conclusions; however, it is possible that the lower CE in

the last run is a result of using the mother liquor which may contain a higher level of impurities.

In four of the five runs conducted, sulfate concentrations detected in the KOH product varied between 1.1mM (100ppm) and 2.1mM (200ppm) corresponding to diffusion coefficients of $1.9 - 2.8 \times 10^{-12} \text{ m}^2/\text{sec}$ and an average of $2.4 \times 10^{-12} \text{ m}^2/\text{sec}$. One of the five runs had a relatively higher rate of diffusion (360ppm and $6.0 \times 10^{-12} \text{ m}^2/\text{sec}$). This result may have been due to experimental error. Note that the level of transport is consistent with that normally seen for bipolar membranes.

The potassium detected in the sulfuric acid product for the runs in the Eurodia stack averaged 143 mg/l, corresponding to an average diffusion coefficient of $2.6 \times 10^{-12} \text{ m}^2/\text{sec}$. However, when the ED-1-BP stack was used, the potassium concentrations increased up to an average of 1035 mg/L corresponding to an average diffusion coefficient of $1.7 \times 10^{-11} \text{ m}^2/\text{sec}$. It is possible that this may have been caused by a slight crossflow leakage of solution.

The ratio of partition coefficients for K vs Na is a measure of the membrane's preference for transporting one species over the other. Measurements of the average K; Na ratios in the feed and the final ratios in the KOH product indicated that they were very consistent for all three runs using the ED-1-BP stack and resulted in an average partition coefficient ratio of 0.93 for K vs Na (FIG's 5 and 6), indicating that the membrane shows very little preference for either species. This is lower than found for Nafion membranes but is very consistent with previous experience gained at ESC. The results obtained when the high Na K_2SO_4 solution was used (Run 484-31) are similar and indicate that the ratio was independent of the relative concentrations of the two species.

Two electrolysis runs were performed, one at $200\text{mA}/\text{cm}^2$ and the other at $350\text{mA}/\text{cm}^2$. The results (see FIGs. 7 and 8) showed that cathodic current efficiencies were consistently high at 98.6% and 98.7%, producing KOH at 4.37M (20.4%) and 7.45M (32%).

In Nafion membranes of 1200 equivalent weight polymer the K:Na coefficient ratio is 3.97;1.22 or 3.25 times that of sodium. Analysis of the anolyte and catholyte solutions before and after electrolysis showed that the ratio of K vs Na increased significantly, indicating that a much purer product was formed, and resulting in an average partition coefficient ratio of 3.75 for K vs. Na into the Nafion membrane.

Based on the partition coefficient ratios obtained for the electrodialysis and electrolysis experiments, it is possible to calculate the maximum concentration of Na impurity that must be present in the starting saturated K_2SO_4 solution. A calculated starting

maximum Na concentration of 6.3ppm Na in 0.7M (13.4%) K_2SO_4 must be achieved in order to produce a 9.27M (40%w/w) solution of KOH with a maximum of 10ppm Na impurity. This level was achieved in saturated solutions prepared from crystals supplied by CPC.

It should also be noted that in the final electrodialysis experiment conducted with solution made from crystal, we were able to produce a KOH solution of sufficient purity required for further electrolysis to produce 9.27M (40%w/w) KOH as specified above. These experiments demonstrate that potassium sulfate solutions can be split into sulfuric acid and potassium hydroxide by electrodialysis using a three compartment cell incorporating bipolar membrane technology. KOH solutions of up to 3.55M(17.2% w/w) can be produced with very good current efficiency (86%) and low sulfate contamination of 1.6M (133ppm) at peak operating current densities of up to 200mA/cm².

There was virtually no preference for transport of potassium vs sodium across the Neosepta CMB cation exchange membrane. The ratio of K vs Na in the feed was very similar to that found in the KOH product. The average partition coefficient ratio for K vs Na was 0.93:1. This is consistent with previous experience gained at ESC. Sulfuric acid at concentrations of up to 1.35M can be produced at current efficient of 76%.

With regard to the electrolysis of reagent grade dilute KOH solutions to produce high purity KOH, Nafion membranes demonstrate a definite preference for the transport of potassium vs sodium. In the experiments performed, up to 7.5M (32%w/w) KOH was made at very high current efficiency of 98.7% and significantly increased purity. The average partition coefficient ratio of K vs Na was 3.75:1.

Using the ratios of partition coefficients obtained during our electrodialysis and electrolysis experiments, we calculate that in order to achieve a final 9.27M (40%w/w) product with 10ppm Na contamination, a starting saturated K_2SO_4 solution of 0.7M (13.4%) must contain 6.3 ppm or less of Na.

It, thus, will be appreciated that the objects of this invention have been fully and effectively accomplished. It will be realized, however, that the foregoing preferred specific embodiment has been shown and described for the purpose of this invention and is subject to change without departure from such principles. Therefore, this invention includes all modifications encompassed within the spirit and scope of the following claims.

What is claimed is:

- 1./ A method for producing high purity colloidal silica comprising the steps of:
providing a quantity of potassium silicate;
subjecting said quantity of potassium silicate stream to an ion exchange
5 process to remove a first portion of potassium therefrom to produce a quantity of colloidal silica; and

subjecting said quantity of colloidal silica to ultrafiltration to remove a portion of sodium therefrom, producing a quantity of high purity colloidal silica.

2. The method of Claim 1, wherein said quantity of potassium silicate has a
10 sodium concentration of less than about 100 ppm.

3. The method of Claim 1, wherein said quantity of colloidal silica has a sodium concentration of less than about 10 ppm.

4. The method of Claim 1, wherein said quantity of high purity colloidal silica has a sodium concentration of less than about 1 ppm.

5. The method of Claim 1, wherein said quantity of colloidal silica consists essentially of silica particles having a size generally between 8 nanometers and 200 nanometers.

6. The method of Claim 1, wherein said ion exchange process step includes the step of contacting said quantity of potassium silicate with a cation exchange resin.

7. The method of Claim 6, wherein said cation exchange resin is selected from the group consisting of carboxylic resins, sulfonated natural materials, and sulfonated styrene-dibenzene copolymers.

8. The method of Claim 1, wherein said ultrafiltration step includes the steps of concentrating said colloidal silica and washing said colloidal silica with deionized water.

9. The method of Claim 8, wherein said ultrafiltration step further includes the step of adding potassium hydroxide to said concentrated colloidal silica to maintain a desired pH and cation concentration.

10. A system for producing high purity colloidal silica comprising:
an ion exchange reactor for receiving a quantity of potassium silicate and
30 removing a portion of potassium therefrom to produce a quantity of colloidal silica; and
an ultrafiltration device for receiving said quantity of colloidal silica and removing a portion of sodium therefrom to produce a quantity of high purity colloidal silica.

11. The system of Claim 10, wherein said quantity of potassium silicate has a sodium concentration of less than about 200 ppm.

12. The system of claim 10, wherein said quantity of colloidal silica has a sodium concentration of less than 10 ppm.

5 13. The system of claim 10, wherein said quantity of high purity colloidal silica has a sodium concentration of less than 1 ppm.

14. The system of Claim 10, wherein said ion exchange reactor includes a cation exchange resin.

10 15. The system of Claim 14, wherein said cation exchange resin is selected from the group consisting of carboxylic resins, sulfonated natural materials, and sulfonated styrene-dibenzene copolymers.

16. The system of Claim 10, wherein said ultrafiltration device includes means for concentrating said colloidal silica and washing said colloidal silica with deionized water.

15 17. The system of Claim 16, wherein said ultrafiltration device further includes means for adding potassium hydroxide to said concentrated colloidal silica to maintain a desired pH and cation concentration.

18. A method for producing high purity colloidal silica and a high purity potassium salt, said method comprising the steps of:

providing a quantity of potassium silicate;

20 subjecting said quantity of potassium silicate to an ion exchange process to remove a first portion of potassium therefrom to produce a quantity of colloidal silica and a potassium enriched ion exchange resin;

subjecting said quantity of colloidal silica to ultrafiltration to remove a portion of sodium therefrom, producing a quantity of high purity colloidal silica;

25 regenerating said potassium rich ion exchange resin with an acid to produce a potassium salt stream; and

subjecting said potassium salt stream to evaporation and crystallization to remove a portion of sodium therefrom to produce a quantity of high purity potassium salt.

30 19. The method of Claim 18, wherein said quantity of colloidal silica has a sodium concentration of less than about 10 ppm.

20. The method of Claim 18, wherein said quantity of high purity colloidal silica has a sodium concentration of less than about 1 ppm.

21. The method of Claim 18, wherein said quantity of high purity potassium salt has a sodium concentration of less than about 10 ppm.

22. A method for producing a high purity potassium hydroxide, said method comprising the steps of:

5 providing a quantity of potassium silicate;

subjecting said quantity of potassium silicate to an ion exchange process to remove a first portion of potassium therefrom to produce a quantity of colloidal silica and a quantity of potassium enriched ion exchange resin;

10 regenerate said quantity of potassium rich ion exchange resin with an acid to produce a quantity of potassium salt;

subjecting said quantity of potassium salt to evaporation and crystallization to remove a portion of sodium therefrom to produce a quantity of high purity potassium salt and

subjecting said quantity of high purity potassium salt to electrodialysis and/or electrolysis to produce a high purity stream of potassium hydroxide.

15

23. The method of Claim 22, wherein said quantity of high purity potassium hydroxide has a sodium concentration of less than about 100 ppm.

24. The method of Claim 22, wherein said quantity of high purity potassium hydroxide salt has a sodium concentration of less than about 10 ppm.

20

25. The method of Claim 22, further including the step of mixing a portion of said quantity of high purity colloidal silica with a portion of said quantity of high purity potassium hydroxide to produce a high purity CMP slurry.

ABSTRACT

A system and method are disclosed for producing high purity colloidal silica by the steps of providing a quantity of potassium silicate; subjecting the quantity of potassium silicate to an ion exchange process to remove a first portion of potassium therefrom to produce a quantity of colloidal silica; and subjecting the quantity of colloidal silica to ultrafiltration to remove a portion of sodium therefrom, producing a quantity of high purity colloidal silica. High purity potassium hydroxide may also be prepared by regenerating the ion exchange resin with an acid to produce a quantity of potassium salt, which may be further purified by evaporation, crystallization, then further processed by electrodialysis and/or electrolysis.

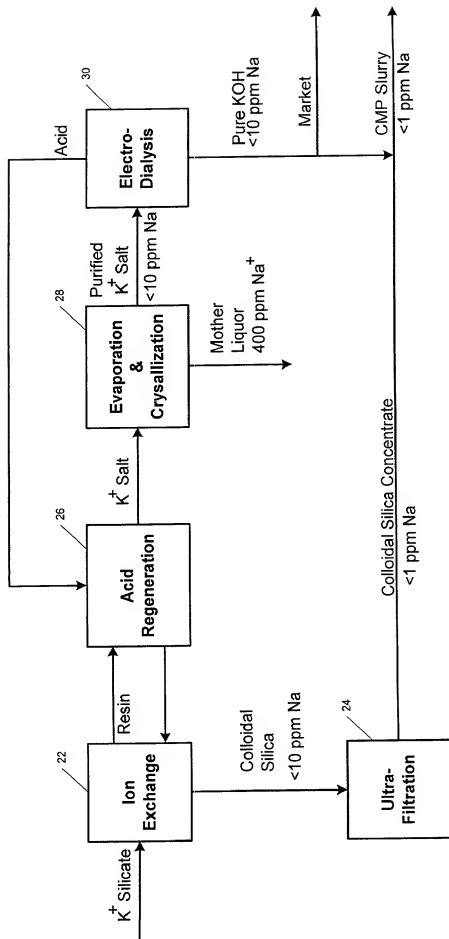


FIG. 1

Membrane Configuration for EUR 2-C-5 Stack.

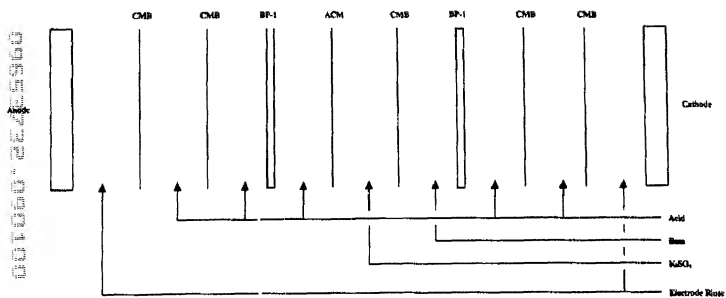


FIG. 2

Membrane Configuration for ED-1 BP Stack.

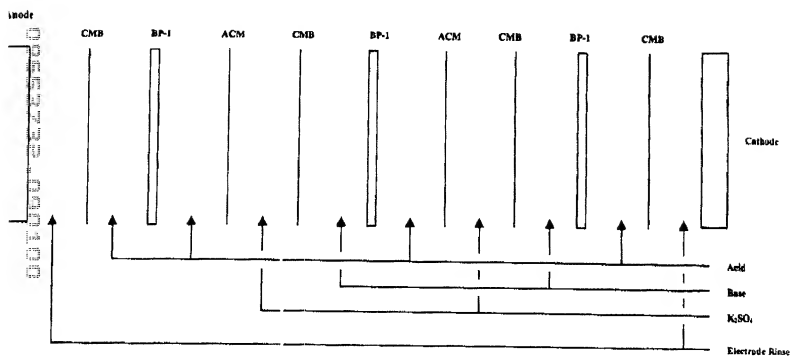


FIG. 3

Summary of ED Runs (K_2SO_4 splitting)

Run#	Cell/Feed Source	Ave CD / V at Peak CD	Init Feed Sulfate Molar	Final Feed Sulfate Molar	Base CE %	Base Cone M KOH / mM SO ₄	Water Transport Into Base Mol/mol K ⁺	Acid CE %	Acid Conc Molar	SO ₄ Mass Balance %
484-2	EUR 2-C-5 / Crystal	84/14.4	0.53	0.33	84	2.28 / 3.8	2.0	74	1.0	99
484-6	EUR 1-C-5 / Crystal	148 / 162	0.75	0.54	87	2.54 / 1.1	3.3	82	1.1	98
484-22	ED-1 BP / Crystal	187 / 13.5	0.70	0.485	84	2.62/1.1	3.9	76	1.35	103
484-27	ED-1 BP / Crystal	162 / 13.3	0.635	0.375	86	3.55 / 1.6	3.1	65	1.33	99
484/31	ED-1 BP / Hi Na	48/20	0.602	0.527	82	1.23/2.1	3.2	50	0.67	96

FIG. 5

Summary of ED Runs (K₂SO₄ splitting)

Run #	K:Na Mole Ratio in Feed	K:Na Mole Ratio in Base	Partition Coefficient across CMB Membrane K vs Na	Diffusion Coefficient SO ₄ m ² /sec	Diffusion Coefficient K into Acid m ² /sec
484-2	-	-	-	6.0*10 ⁻¹²	2.7*10 ⁻¹²
484-6	-	-	-	1.9*10 ⁻¹²	3.1*10 ⁻¹²
484-22	6405:1	5468:1	0.9	2.3*10 ⁻¹²	2.4*10 ⁻¹²
484-27	8596:1	9561:1	1.1	2.5*10 ⁻¹²	1.6*10 ⁻¹²
484-31	57:1	45:1	0.8	2.8*10 ⁻¹²	1.2*10 ⁻¹²

FIG. 6
Summary of Analytical Results for ED Runs

Run	Initial Feed [Na] / [SO ₄] / pH Mg/L / M / pH	Final Feed [Na] / [SO ₄] / pH Mg/L / M / pH	Initial Base [Na] / [OH] / [SO ₄] Mg/L / M / M	Final Base [Na] / [OH] / [SO ₄] Mg/L / M / M	Initial Acid [SO ₄] / [K] M / mg/L	Final Acid [SO ₄] / [K] M / mg/L
484-6	15 / 0.528 / -	21 / 0.332 / 1.7	1 / 0 / 0	133 / 2.28 / 0.0038	0.5 / 11	1.0 / 127
484-6	9 / 0.750 / 7.5	13 / 0.542 / 2.4	2 / 0 / 0	49 / 2.54 / 0.0011	0.5 / 11	1.1 / 159
484-22	5.5 / 0.698 / 8.5	3.2 / 0.485 / 1.8	0 / 0 / 0	20 / 2.62 / 0.0011	0.582 / 11	1.35 / 1237
484-27	3.6 / 0.635 / 7.5	1.9 / 0.375 / 1.4	0 / 0 / 0	20 / 3.55 / 0.0016	0.472 / 11	1.33 / 1084
484-31	511 / 0.602 / 10.3	403 / 0.527 / 2.0	0 / 0 / 0	349 / 1.23 / 0.0021	0.486 / 11	0.665 / 783

FIG. 7

Summary KOH Electrolysis

Run #	CD/V mA/cm ² / V	Charge Passed	Unit Anolyte [OH] M	Unit Catholyte [OH] M	Final Catholyte [OH] M / %	Cathodic CE %	K:Na mole Ratio in Anolyte	K:Na mole Ratio Transported across Membrane	Partition Coefficient For K vs Na
484.11	200 / 4.6	2.75 F	2.54	0.1	4.37 / 20.4	98.6	1544:1	6273:1	4.1
484.15	340 / 5.6	2.48	2.52	4.05	7.45 / 32.0	98.7	1617:1	5457:1	3.4

FIG. 8

Summary of Analytical Results for Electrolysis Runs

RUN #	Initial Anolyte [OH] / [Na] M / mg/L	Final Anolyte [OH] / [Na] M / mg/L	Initial Catholyte [OH] / [Na] M / mg/L	Final Catholyte [OH] / [Na] M / mg/L
484-11	2.54 / 29	1.18 / 25.3	0 / 0	4.37 / 16
484-15	2.52 / 29.4	1.38 / 25.8	4.05 / 19.4	7.45 / 33.6

In Re Application: ANDREW JOSEPH PASZKOWSKI
DECLARATION AND POWER OF ATTORNEY

Attorney's Docket No. 011916.107912

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am an original, first and sole inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled: **SYSTEM AND METHOD FOR PRODUCING HIGH PURITY COLLOIDAL SILICA AND POTASSIUM HYDROXIDE**, the specification of which:

☒ is attached hereto.

☐ was filed on _____ as Application No. _____ (if applicable) and was amended on _____.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I do not know and do not believe that the same was ever known or used by others in the United States of America before my invention thereof, or patented or described in any printed publication in any country before my invention thereof or more than one year prior to the date of this application. I further state that the invention was not in public use or on sale in the United States of America more than one year prior to the date of this application. *I understand that I have a duty of candor and good faith toward the Patent and Trademark Office*, and I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(d) of the foreign application(s) for patent or inventor's certificate listed below, and have also identified below any foreign application for patent or inventor's certificate disclosing subject matter in common with the above-identified specification and having a filing date before that of the application on which priority is claimed:

Application No.	Country	Filing Date	Priority Claimed Under 35 USC §119
None			Yes _____ No _____

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter disclosed and claimed in the present application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status: patented, pending, abandoned
None		

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patents issuing thereon.

POWER OF ATTORNEY: The following attorneys and/or agents are hereby appointed to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: GERALD R. BOSS, REG. NO. 36,460; R. STEVAN COURSEY, REG. NO. 39,949; TODD DEVEAU, REG. NO. 29,526; JOEL S. GOLDMAN, REG. NO. 29,070; W. BROOK LAFFERTY, REG. NO. 39,259; HAROLD L. MARQUIS, REG. NO. 20,594; RYAN A. SCHNEIDER, REG. NO. 45,083; GREGORY S. SMITH, REG. NO. 40,819; KENNETH SOUTHALL, REG. NO. 38,315; CHARLES L. WARNER, REG. NO. 32,320; and ROGER S. WILLIAMS, REG. NO. P43,273.

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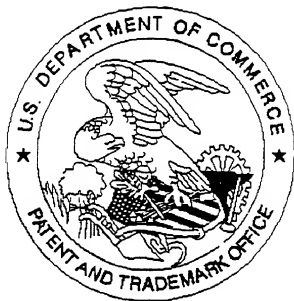
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